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# XIV, Part 1: Incorporation of water into glasses and its influence on the diffusion of cations, including the creation of diffusion barriers

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# **Incorporation of Water into Glasses and its Influence on the Diffusion of Cations, Including the Creation of Diffusion Barriers**

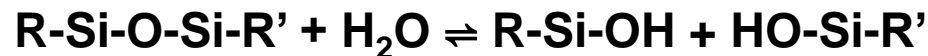
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# Water in Silicate Glasses I

- **how is water accommodated?**

- most in the form of OH groups, little in the form of water molecules
- OH groups are formed by reaction between water molecules and the glass network by the reaction



- **how much water can be accommodated in glasses?**

- depends on several parameters:
  - purity of the raw materials used for making the glass
  - chemical composition of the glass
  - thermal history of the glass
  - annealing conditions, i.e., temperature, total pressure, water vapor pressure
  - sample geometry
  - time of annealing
- sample may or may not be completely equilibrated during annealing, the latter leading to a non-uniform water distribution
- very large water contents are possible

# Water in Silicate Glasses II

- **processes involved in the incorporation of water into glass?**
  - transport of  $\text{H}_2\text{O}$  molecules within the surrounding atmosphere to the gas/glass interface; occurs usually very fast and has therefore in most cases no influence on the overall reaction rate
  - reaction at the gas/glass interface, e.g.,  $\text{H}_2\text{O}_{(\text{gas})} \rightleftharpoons \text{H}_2\text{O}_{(\text{glass})}$
  - transformation of  $\text{H}_2\text{O}$  into OH groups within the glass, i.e., the reaction  $\text{R-Si-O-Si-R}' + \text{H}_2\text{O} \rightleftharpoons \text{R-Si-OH} + \text{HO-Si-R}'$
  - transport within the glass, i.e., diffusion of  $\text{H}_2\text{O}$  molecules and of OH groups; usually the diffusion of  $\text{H}_2\text{O}$  molecules is much faster than that of OH groups
- **kinetics of water uptake during annealing at high temperatures?**
  - depend on the rates of the reactions denoted above and on the diffusivities of water-related species in the glass
  - limiting cases: diffusion control and reaction control

# How to Measure the Water Content of Glasses?

- $c_{\text{OH}} \gg c_{\text{H}_2\text{O}}$ ; therefore measure only  $c_{\text{OH}}$
- IR absorption due to OH stretching vibration at a wavenumber of about  $3600 \text{ cm}^{-1}$
- intensity of this absorption is related to the concentration of OH and to the overall water concentration
- absorption due to OH groups is described by the Beer-Lambert law:  

$$I \approx I_0 \cdot e^{-\alpha_{\text{OH}} \cdot c_{\text{OH}}^m \cdot \ell_g}$$

$$I \approx I_0 \cdot 10^{-\epsilon_{\text{OH}} \cdot c_{\text{OH}}^m \cdot \ell_g} = I_0 \cdot 10^{-A_g}$$
- relation between the absorbance  $A_g$  and the concentration of OH groups:

$$A_g = -\log \frac{I}{I_0} = c_{\text{OH}} \cdot \epsilon_{\text{OH}} \cdot \ell_g \cdot \frac{\rho_g}{M_{\text{OH}}} = 2 c_{\text{H}_2\text{O}} \cdot \epsilon_{\text{OH}} \cdot \ell_g \cdot \frac{\rho_g}{M_{\text{H}_2\text{O}}} = c_{\text{H}_2\text{O}} \cdot \epsilon_{\text{H}_2\text{O}} \cdot \ell_g \cdot \frac{\rho_g}{M_{\text{H}_2\text{O}}}$$

- $\epsilon_{\text{OH}}$  = molar absorption coefficient related to the overall concentration of OH groups present in the glass ( $\ell/(\text{mol}_{\text{OH}} \cdot \text{cm})$ )
- $\ell_g$  = thickness of glass sample (cm)
- $c_{\text{OH}}^m$  = molar concentration of OH
- $A_g$  = absorbance
- $c_{\text{OH}}, c_{\text{H}_2\text{O}}$  = mass fractions of OH,  $\text{H}_2\text{O}$
- $M_{\text{OH}}, M_{\text{H}_2\text{O}}$  = molar masses of OH,  $\text{H}_2\text{O}$
- $\rho_g$  = density of the glass ( $\text{g}/\text{cm}^3$ )
- $I/I_0$  = ratio between transmitted and initial IR signal
- $\epsilon_{\text{H}_2\text{O}}$  = molar absorption coefficient related to the overall concentration of  $\text{H}_2\text{O}$  in the glass ( $\ell/(\text{mol}_{\text{H}_2\text{O}} \cdot \text{cm}) = 2 \epsilon_{\text{OH}}$ )

# FTIR Measurement of the OH-Content of Glasses

- from the Beer-Lambert law:

$$c_{\text{H}_2\text{O}} = \frac{M_{\text{H}_2\text{O}}}{m_{\text{glass}}} = \frac{1}{2} \cdot \frac{A_g}{\epsilon_{\text{OH}} \cdot \ell_g} \cdot \frac{M_{\text{H}_2\text{O}}}{\rho_g}$$

with

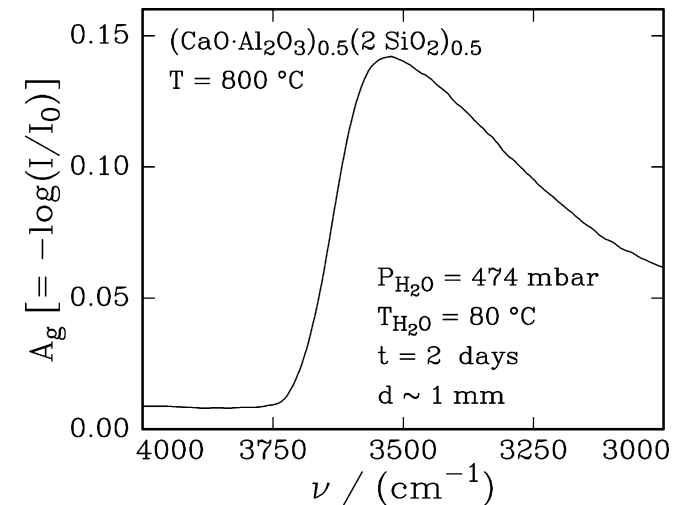
$$A_g = -\log_{10} \left( \frac{I}{I_0} \right)$$

- reorganization of the equation for  $c_{\text{H}_2\text{O}}$ :

$$c_{\text{H}_2\text{O}} \cdot \epsilon_{\text{OH}} = \frac{1}{2} \cdot \frac{A_g}{\ell_g} \cdot \frac{M_{\text{H}_2\text{O}}}{\rho_g}$$

- change in the  $\text{H}_2\text{O}$  concentration after annealing for the time  $t$ :

$$\Delta c_{\text{H}_2\text{O}} = c_{\text{H}_2\text{O}}(t) - c_{\text{H}_2\text{O}}(t = 0)$$



- $\epsilon_{\text{OH}}$  = molar absorption coefficient related to the overall concentration of OH groups present in the glass ( $\ell/(\text{mol}_{\text{OH}} \cdot \text{cm})$ )
- $\ell_g$  = thickness of glass sample (cm)
- $c_{\text{H}_2\text{O}}$  = mass fraction of  $\text{H}_2\text{O}$
- $M_{\text{H}_2\text{O}}$  = molar mass of  $\text{H}_2\text{O}$  (= 18 g/mol)
- $\rho_g$  = density of the glass ( $\text{g}/\text{cm}^3$ )
- $I/I_0$  = ratio between transmitted and initial IR signal

# Structural Changes Upon the Uptake of Water — Structural Relaxation

- **structural changes due to the uptake of water:**

- water molecules accommodated as such may cause local changes in the spacing between glass components
- the formation of OH-groups by the reaction  $\text{R-Si-O-Si-R}' + \text{H}_2\text{O} \rightleftharpoons \text{R-Si-OH} + \text{HO-Si-R}'$  may also lead to local structural changes
- more important: the dynamical nature of the equilibrium reaction denoted above
  - temporary formation of OH-groups and subsequent formation of  $\text{H}_2\text{O}$  molecules enables the glass network to undergo a structural relaxation
  - long range structural changes can take place, leading to changes in bonding angles and distances
  - for silica glass experimentally confirmed by Tomozawa and his group that such structural changes occur

- **expectation:**

all structure-sensitive properties of glasses (e.g., viscosities, diffusivities, etc.) change when structural changes occur due a water uptake

# Opportunity for Generating Functionally Graded Glass?

- if the uptake of water leads to useful property changes, water incorporation can be used to generate glass with properties changing as a function of the distance from the surface
  - low tech approach
  - low cost
- by annealing glass in a moist atmosphere at high temperature the properties of the near-surface region may be changed while the rest of the glass remains unchanged
- example of interest here:
  - modification of the diffusivity of ions by the incorporation of water
  - can be used to generate a diffusion barrier if the diffusivity of interest in the water uptake-influenced region is significantly smaller than in the rest of the sample



# Silicate Glasses of Interest

- **Type I silica (Heraeus Infrasil 302)**

- fused quartz made by melting of natural quartz crystals
- average concentration of metallic impurities: about 40 ppm by weight
  - ◇ most abundant: Al (about 30 ppmw)
  - ◇ Ti, Fe and Na present at the one ppmw level
  - ◇ OH content less than 8 ppmw
- strain point: 1075 °C

- **Corning Code 1737 glass**

- alkaline earth boroaluminosilicate glass
- composition (in mol %): SiO<sub>2</sub> 69.0 %, Al<sub>2</sub>O<sub>3</sub> 11.5 %, B<sub>2</sub>O<sub>3</sub> 7.3 % CaO 5.0 %, BaO 4.4 %, MgO 1.4 %, SrO 1.2 % and As<sub>2</sub>O<sub>3</sub> 0.2 %, Na impurity level 600 ppma; OH about 500 ppmw
- fusion drawn substrate glass for flat panel display applications
- strain point 666 °C

- **model glasses of the type  $(\text{CaO} \cdot \text{Al}_2\text{O}_3)_{1-x} (2 \text{SiO}_2)_x$**

# Topics of Interest

- **questions:**

- how fast is water taken up?
- which type of kinetics determines the water uptake?
- how large are the diffusion rates of sodium cations in general?
- how are these rates influenced by water taken up during pre-annealing and/or during diffusion annealing?
- can the uptake of water by a glass produce something useful, e.g., be used to generate barrier layers?
- if yes, how effective are such barrier layers?

- **experiments:**

- infrared absorption studies on the integral rate of the water uptake
- tracer diffusion experiments with Na-22

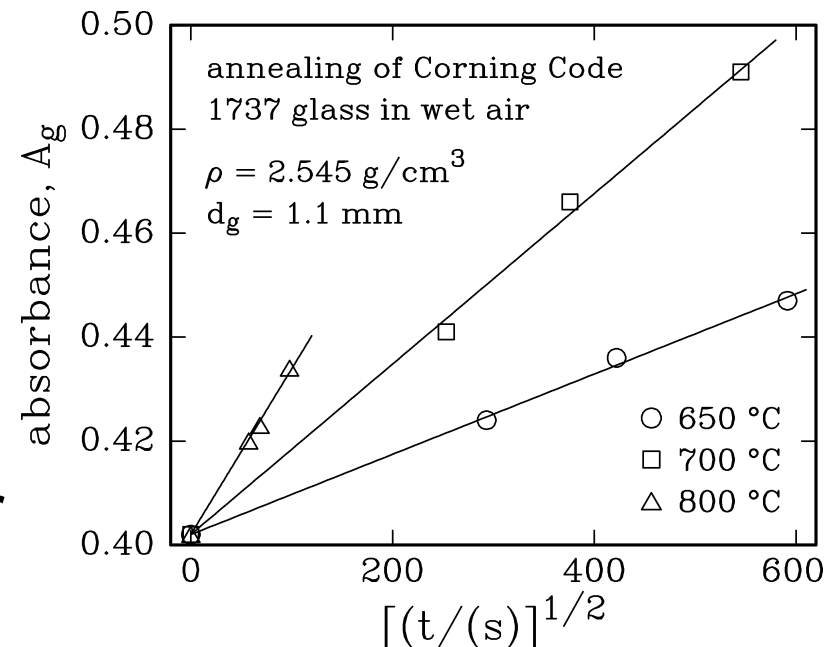
# Water Uptake by Corning Code 1737 Glass I

- **experiments:**

- annealing of glass samples for different times in wet air (air saturated with water at 80 °C) at 650, 700 and 800 °C
- measurement of the absorbance related to OH groups

- **results:**

- analysis of the time dependence of the absorbance shows that it increases with the square root of the annealing time
- indicates that the uptake of water is a diffusion-controlled process



# Water Uptake by Corning Code 1737 Glass II

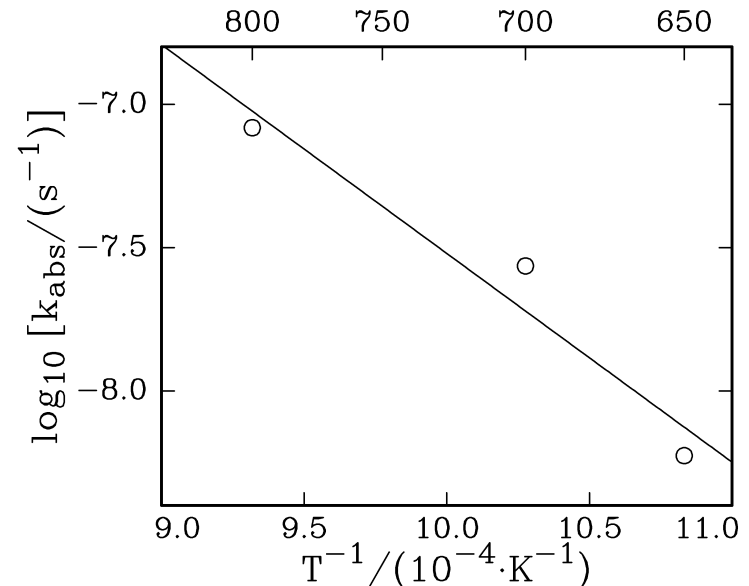
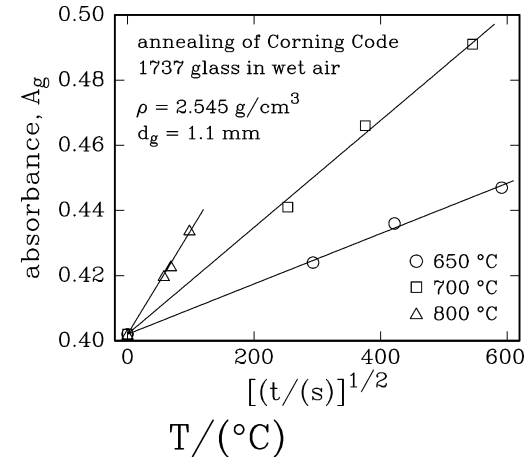
## • water content:

- absorbance observed at  $t = 0$  corresponds to an OH concentration of about 500 ppm by weight
- estimated that the OH concentrations at the glass surface could be about 20 times higher at 650, 700 and 800 °C in wet air

## • kinetics:

- time dependence of absorbance:  

$$A_g(t) = A_g(t=0) + (k_{\text{abs}} \cdot t)^{1/2}$$
- $k_{\text{abs}}$  obtained from the slopes in the plot shown before
- T-dependence of  $k_{\text{abs}}$ : activation energy =  $139.5 (\pm 34.5)$  kJ/mol; to be attributed to the diffusion of  $\text{H}_2\text{O}$



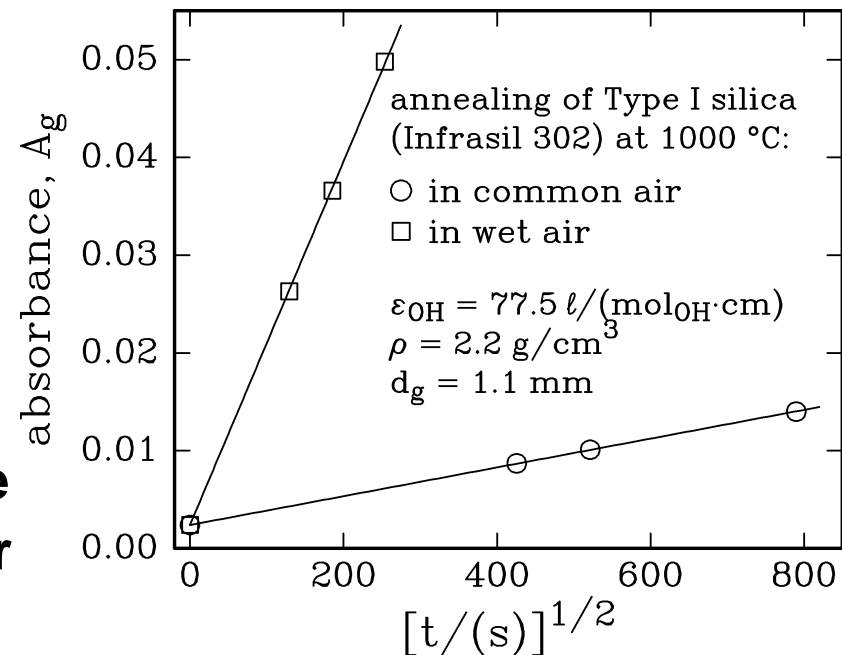
# Water Uptake by Type I Silica Glass (Infrasil 302) I

- **experiments:**

- annealing of glass samples for different times in wet and common air (air saturated with water at 80 °C) at 1000 °C
- measurement of the absorbance related to OH groups

- **results:**

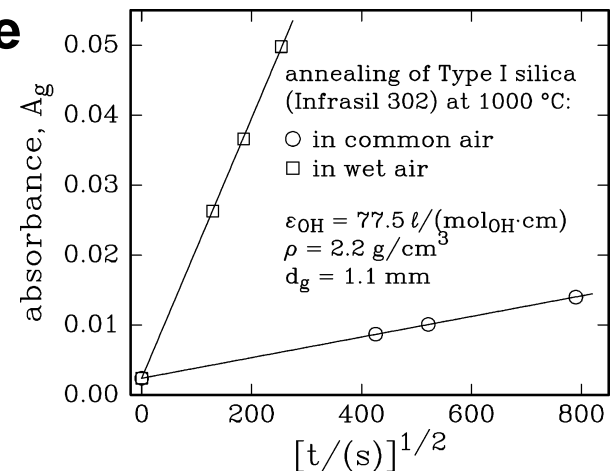
- analysis of the time dependence of the measured absorbance shows that the absorbance increases as function of the square root of the annealing time
- indicates that the uptake of water is a diffusion-controlled process



# Water Uptake by Type I Silica Glass (Infrasil 302) II

- **water content:**

- absorbance observed at  $t = 0$  corresponds to an OH concentration of about 2 ppm by weight
- estimated that the OH concentrations at the glass surface could be about 160 and 800 ppm by weight in common and in wet air, respectively
- OH concentration ratio is in good agreement with that expected based on equilibrium water pressures at 18 and 80 °C



- **kinetics:**

- time dependence of the absorbance:  $A_g(t) = A_g(t=0) + (k_{abs} \cdot t)^{1/2}$
- values for  $k_{abs}$  obtained from the slopes in the plot shown before
- $k_{abs}(\text{wet air})/k_{abs}(\text{common air}) \approx 160$ , i.e., much larger than the corresponding  $P_{H_2O}$ -ratio; the reason for this is unknown

# Sodium Diffusion Profiles I

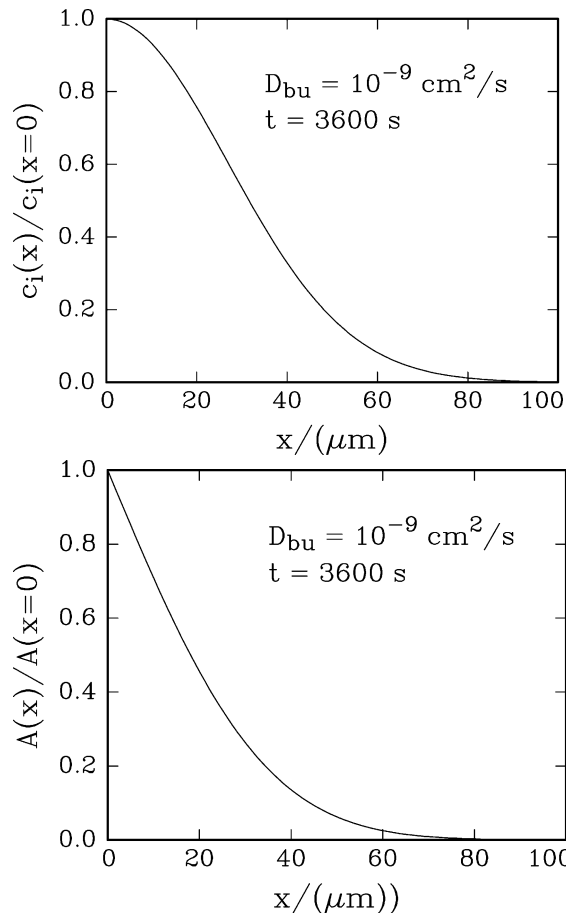
- radioactive tracer (Na-22) always applied as a thin film
- in all diffusion experiments residual radioactivity profiles measured
- after diffusion annealing, residual radioactivity profiles determined, i.e., residual radioactivity measured after the successive removal of sample material beginning at the surface where tracer was applied
- different types of concentration profiles observed after diffusion-annealing, different solutions of Fick's 2<sup>nd</sup> law apply for  $c_i(x,t)$  ( $i = \text{Na-22}$ )
- residual radioactivity after removal of material of the thickness  $x$ :

$$\frac{A(x)}{A(x=0)} = \frac{\int_x^{\infty} c(x) \cdot dx}{\int_0^{\infty} c(x) \cdot dx} = f(x, t)$$

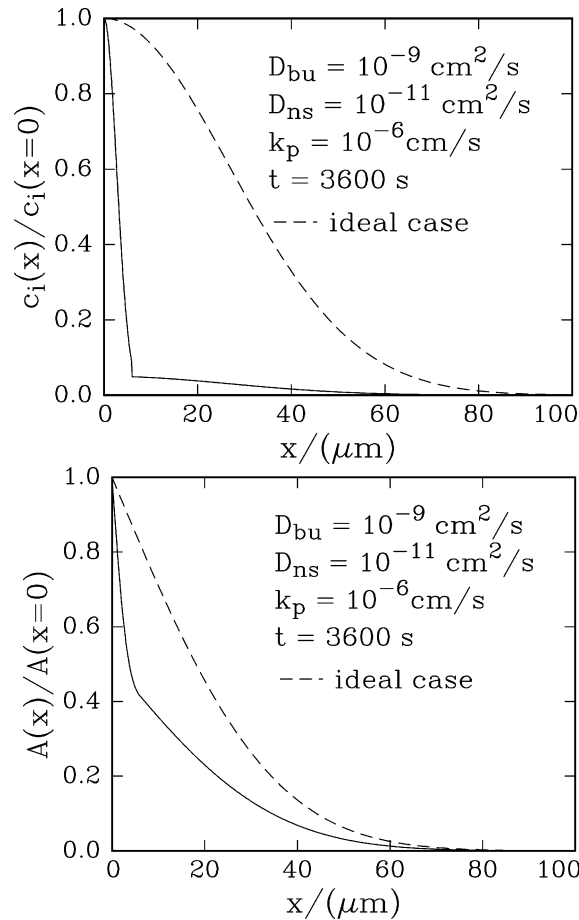
- in the following, discussion of different cases of relevance

# Sodium Diffusion Profiles II

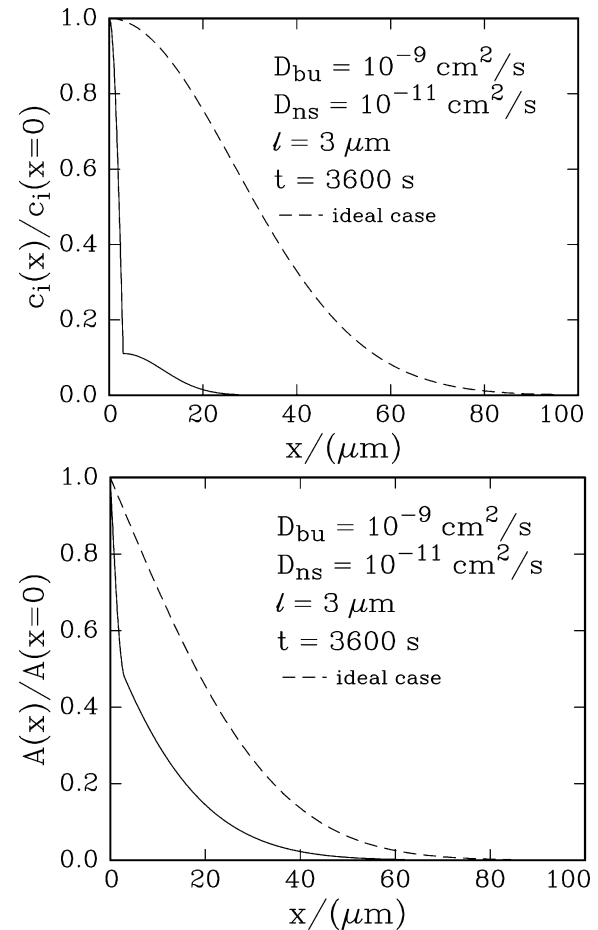
## • profiles for Case A:



## • profiles for Case B:



## • profiles for Case C:





# Sodium Diffusion Profiles III

- if the samples are homogeneous with regard to their chemical composition and their structure, the thin film solution of Fick's 2<sup>nd</sup> law applies

$$c_i(x,t) = \frac{Q_i}{\sqrt{\pi \cdot D_i \cdot t}} \cdot \exp\left(-\frac{x^2}{4 D_i \cdot t}\right)$$

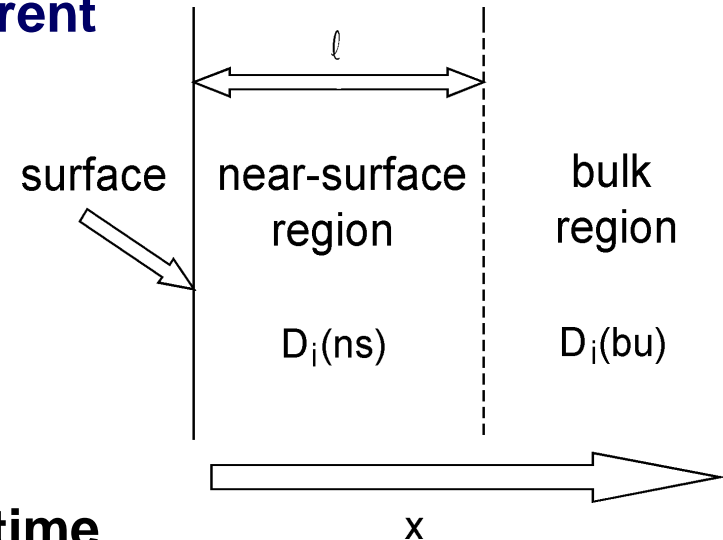
- residual radioactivity after removal of material of the thickness x:

$$\frac{A(x)}{A(x=0)} = \frac{\int_x^\infty c(x) \cdot dx}{\int_0^\infty c(x) \cdot dx} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{D_i \cdot t}}\right)$$

- in the following, this case will be denoted as Case A

# Sodium Diffusion Profiles IV

- if the samples are inhomogeneous, different solutions of Fick's 2<sup>nd</sup> law need to be applied
- considered are samples with a near-surface region, in which the diffusion rate is different from that in the bulk, i.e.,  $D_i(\text{ns}) \neq D_i(\text{bu})$
- two cases of interest:
  - **Case B:** thickness of the near-surface region,  $\ell$ , changes with the diffusion-annealing time,  $\ell = (k_{p(\text{da})} \cdot t_{\text{da}})^{1/2}$
  - **Case C:** thickness of the near-surface region,  $\ell$ , does not change with the diffusion-annealing time (but with the time of pre-annealing at a significantly higher temperature than that of the diffusion anneal, i.e.,  $\ell = (k_{p(\text{pa})} \cdot t_{\text{pa}})^{1/2}$ )
- different solutions for  $x < \ell$  and for  $x > \ell$



# Sodium Diffusion Profiles V

- solution for Case B:

- for  $x < \ell$ :

$$\frac{A(x < \ell)}{A(x = 0)} = 1 - \frac{\operatorname{erf}\left(\frac{x}{2\sqrt{D_{ns} \cdot t}}\right)}{\operatorname{erf}\left(\frac{1}{2}\sqrt{\frac{k_{p(da)}}{D_{ns}}}\right) + \sqrt{\frac{D_{bu}}{D_{ns}}} \cdot \exp\left(\frac{k_{p(da)}}{4D_{bu}} - \frac{k_{p(da)}}{4D_{ns}}\right) \cdot \operatorname{erfc}\left(\frac{1}{2}\sqrt{\frac{k_{p(da)}}{D_{bu}}}\right)}$$

- for  $x > \ell$ :

$$\frac{A(x > \ell)}{A(x = 0)} = \frac{\operatorname{erfc}\left(\frac{x}{2\sqrt{D_{bu} \cdot t}}\right)}{\operatorname{erfc}\left(\frac{1}{2}\sqrt{\frac{k_{p(da)}}{D_{bu}}}\right) + \sqrt{\frac{D_{ns}}{D_{bu}}} \cdot \exp\left(\frac{k_{p(da)}}{4D_{ns}} - \frac{k_{p(da)}}{4D_{bu}}\right) \cdot \operatorname{erf}\left(\frac{1}{2}\sqrt{\frac{k_{p(da)}}{D_{ns}}}\right)}$$

- solution for Case C:

- for  $x < \ell$ :

$$\frac{A(x < \ell)}{A(x = 0)} = \operatorname{erf}\left[\frac{x}{2\sqrt{D_{Na}^*(ns) \cdot t}}\right] \cdot \sum_{n=0}^{\infty} \lambda^{n+1} \cdot \left( \operatorname{erf}\left[\frac{(2n+2) \cdot \ell + x}{2\sqrt{D_{Na}^*(ns) \cdot t}}\right] - \operatorname{erf}\left[\frac{(2n+2) \cdot \ell - x}{2\sqrt{D_{Na}^*(ns) \cdot t}}\right] \right)$$

- for  $x > \ell$ :

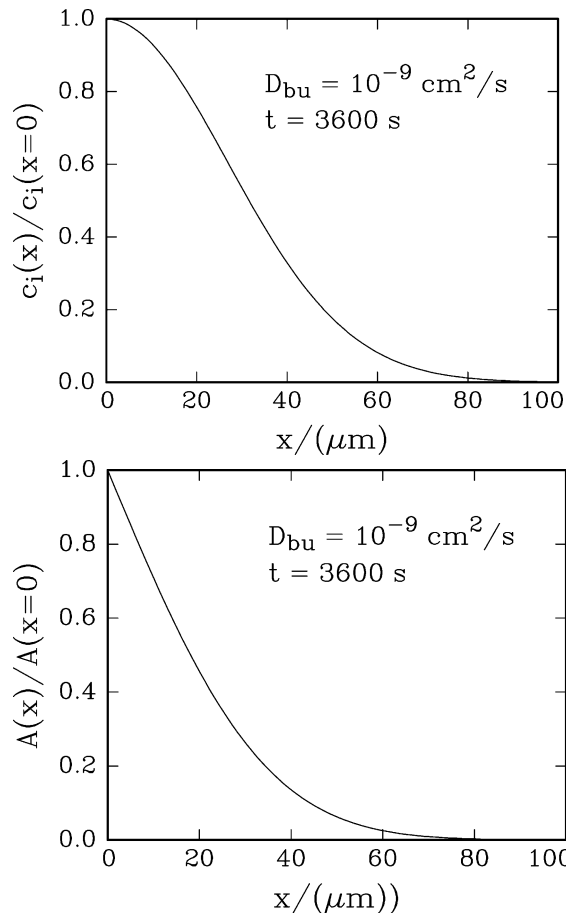
$$\frac{A(x > \ell)}{A(x = 0)} = \frac{2\alpha}{\alpha + 1} \cdot \sum_{n=0}^{\infty} \lambda^n \cdot \operatorname{erfc}\left[\frac{(2n+1) \cdot \ell + \alpha^{-1} \cdot (x - \ell)}{2\sqrt{D_{Na}^*(ns) \cdot t}}\right]$$

where

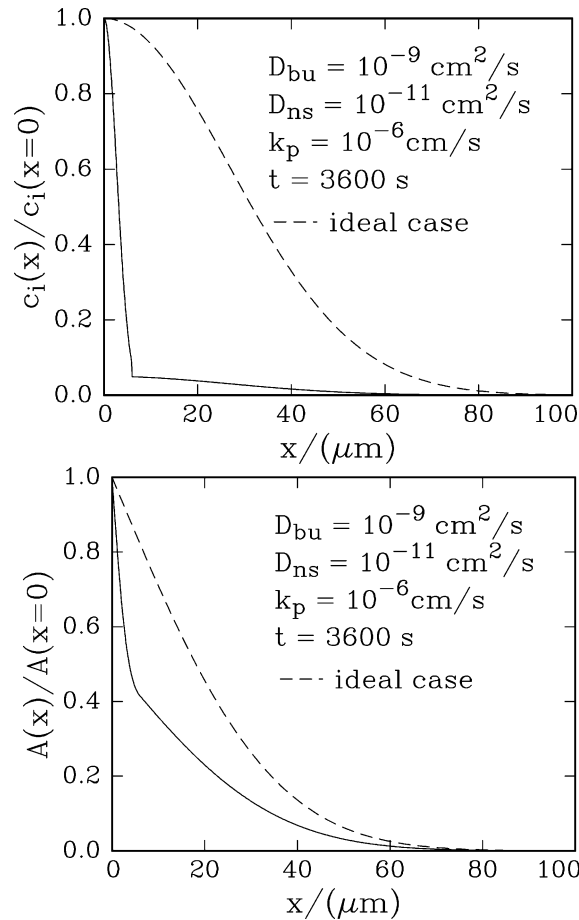
$$\alpha = \sqrt{\frac{D_{Na}^*(bu)}{D_{Na}^*(ns)}} \quad \text{and} \quad \lambda = \frac{1 - \alpha}{1 + \alpha}$$

# Sodium Diffusion Profiles VI

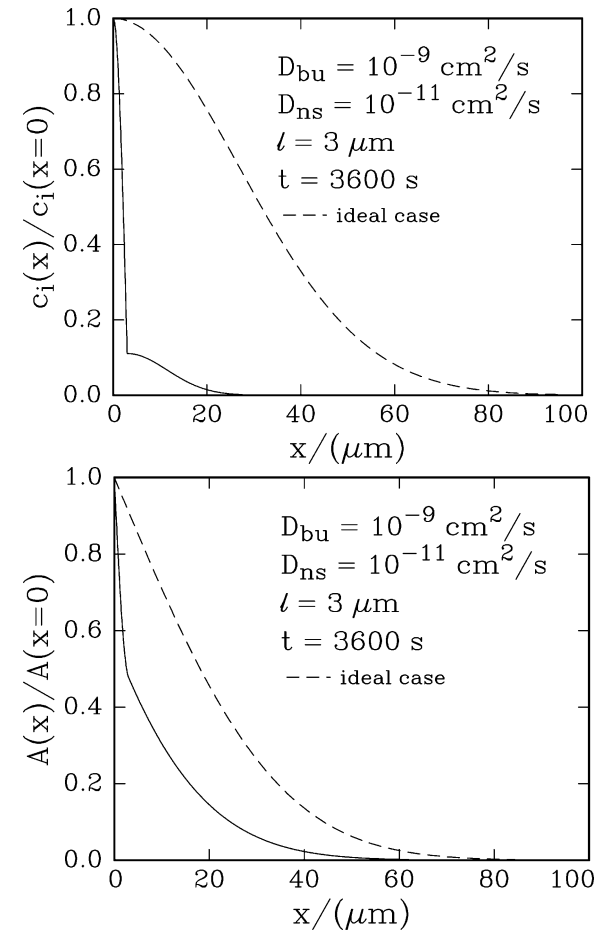
## • profiles for Case A:



## • profiles for Case B:

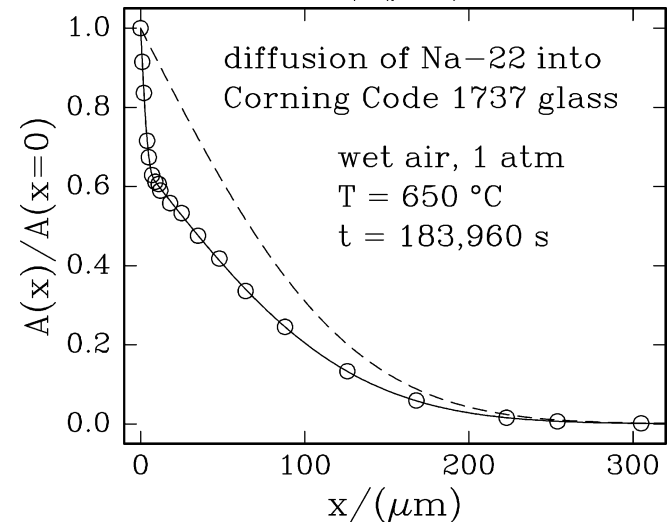
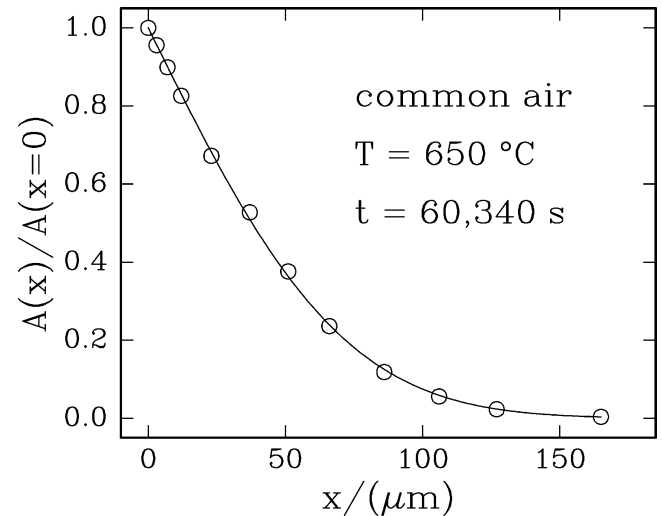


## • profiles for Case C:



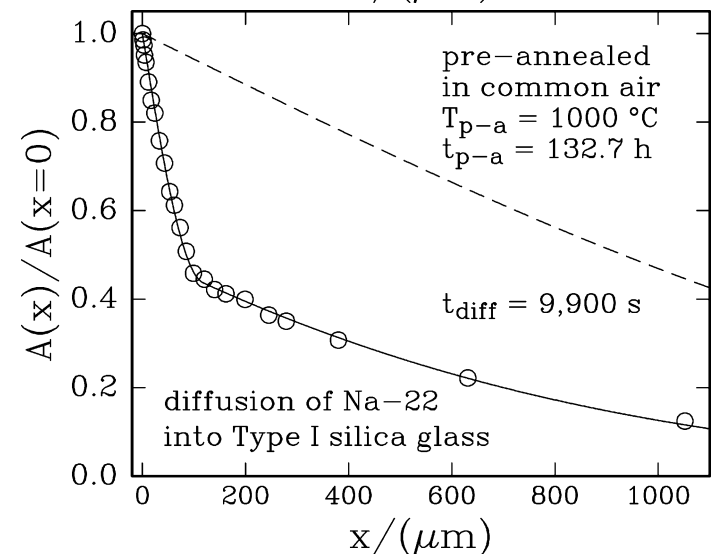
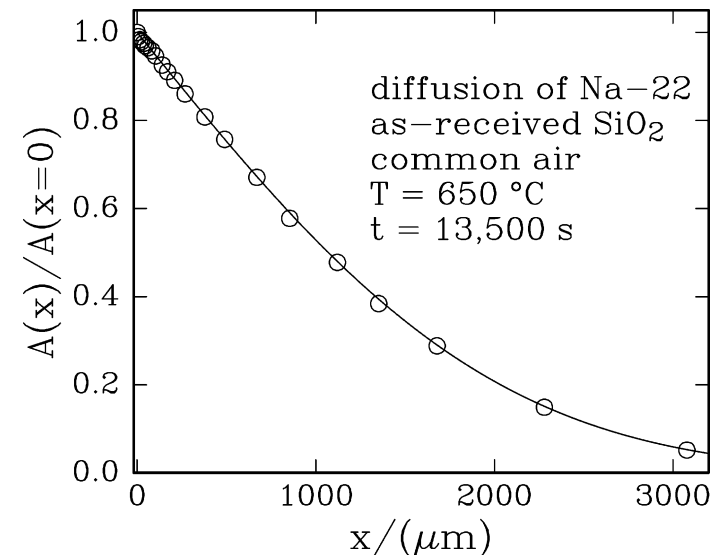
# Diffusion of Na in 1737 Glass I

- diffusion-annealing of as-received samples in dry and in common air leads to type A profiles, i.e., to profiles that can be described by a single diffusion coefficient
- type B profiles with kinks are observed after diffusion-annealing of as-received samples in wet air (i.e., air saturated with  $\text{H}_2\text{O}$  at  $80^\circ\text{C}$ )
- the location of the kink changes with the diffusion-annealing time
- the kink displacement with the diffusion-annealing time follows a parabolic rate law, as assumed for type B profiles
- the presence of sharp kinks justifies the assumption that  $D_{\text{Na}}(\text{ns})$  is constant



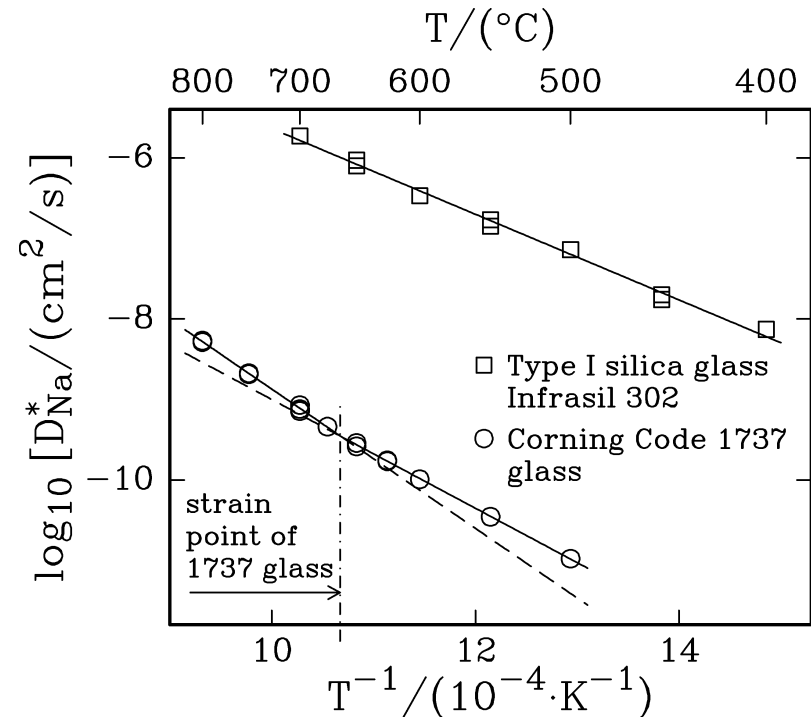
# Na Diffusion in Type I Silica Glass I

- type A profiles are observed in Na-22 diffusion experiments in common and wet air at lower temperatures with as-received samples of Infrasil 302
- if the samples are pre-annealed at higher temperatures (900 - 1100 °C) in common or wet air, kinks are observed in tracer diffusion profiles generated at much lower temperature (650 °C), i.e., type C profiles are obtained
- the location of the kink,  $\ell$ , as a function of the pre-annealing time follows a parabolic rate law



# Comparison of Bulk Diffusion Coefficients

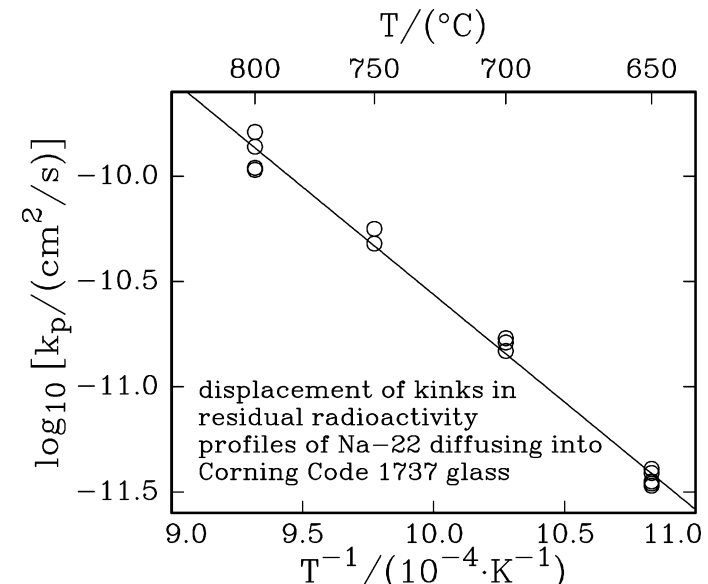
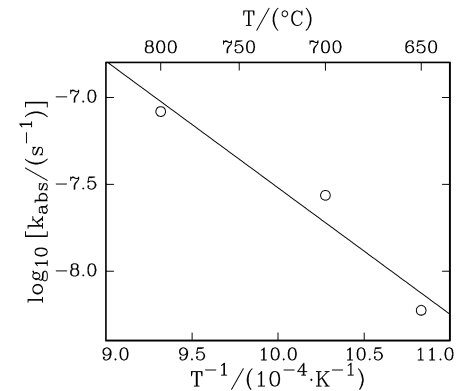
- a comparison of sodium tracer diffusion coefficients obtained from Type A profiles is shown at the right
- sodium diffusion occurs in Type I silica glass much faster than in Corning Code 1737 glass
- a simple Arrhenius-type temperature dependence is found the diffusion of Na-22 in Type I silica glass (Infrasil 302);  $E_a = 101.8 \pm 2.7$  kJ/mol
- change in temperature dependence of the diffusion of Na-22 in 1737 glass at the strain point of this glass; two Arrhenius expressions needed to describe the temperature dependence of the sodium diffusion



- activation energies for Na diffusion in 1737 glass:
  - high T:  $165.5 \pm 3.0$  kJ/mol
  - low T:  $129.9 \pm 1.2$  kJ/mol

# Kink Displacement in Na Diffusion Profiles in Corning Code 1737 Glass Obtained After Diffusion-Annealing in Wet Air

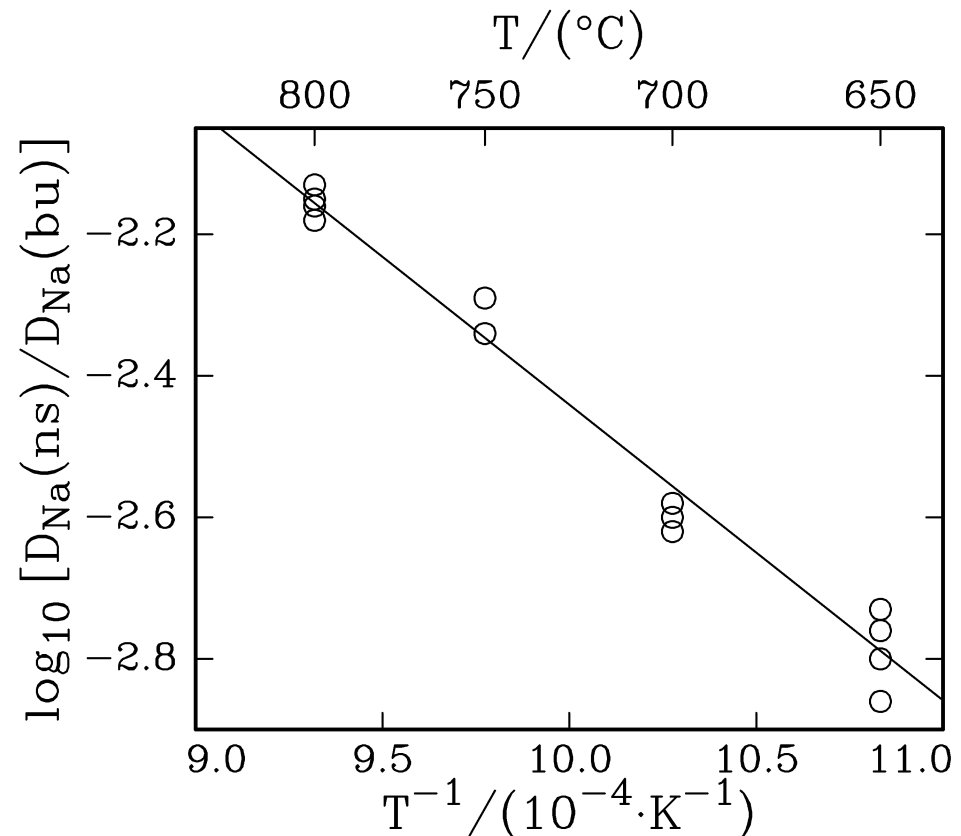
- discussed before that the integral water uptake of 1737 glass during annealing in wet air follows a parabolic rate law, i.e., that it is diffusion-controlled
- $E_a = 139.4 (\pm 34.4)$  kJ/mol for the water uptake; is related to the diffusion of  $H_2O$
- kink displacement observed in diffusion profiles after diffusion-annealing in wet air follows also a parabolic rate law
- $E_a = 195.6 (\pm 5.2)$  kJ/mol for the kink displacement
- the difference between the two activation energies must be related to structural changes occurring upon the incorporation of water





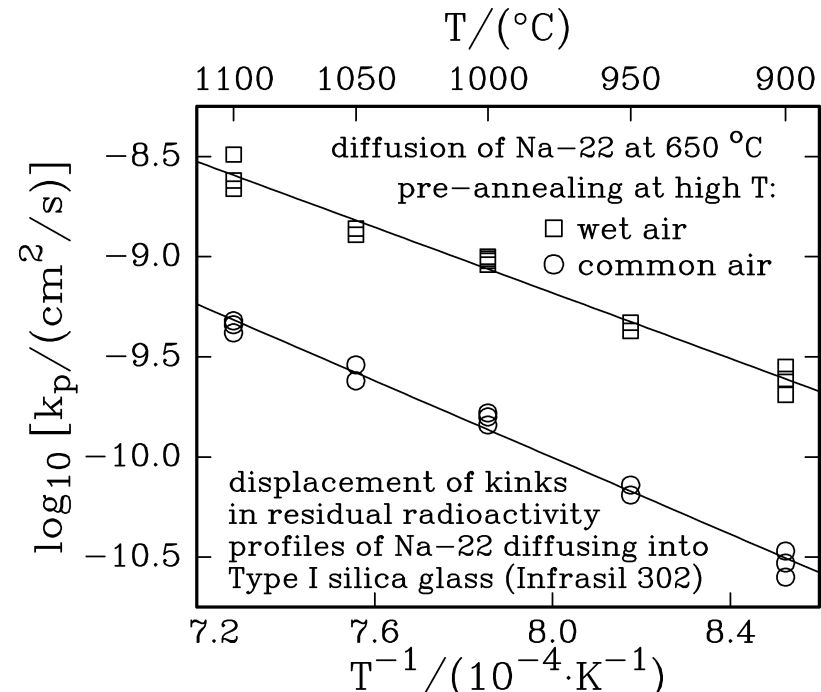
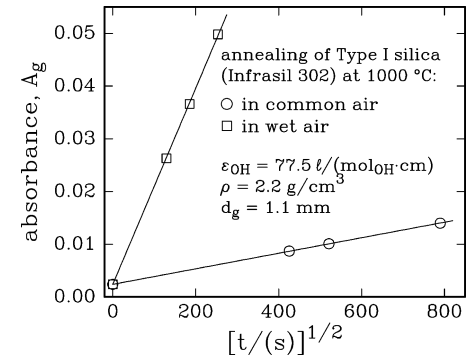
# Comparison Between the Diffusion Rate of Na in the Near-Surface Region and in the Bulk of 1737 Glass

- reduction of the  $\text{Na}^+$  diffusion rate near the surface due to the uptake of water
- $D_{\text{Na}}(\text{ns})$  100 to 1000 times smaller than  $D_{\text{Na}}(\text{bu})$  (ns = near the surface, bu = bulk)
- only little scatter in the ratio  $D_{\text{Na}}(\text{ns})/D_{\text{Na}}(\text{bu})$
- no time dependence of the ratio  $D_{\text{Na}}(\text{ns})/D_{\text{Na}}(\text{bu})$ , i.e., structural changes upon the uptake of water must occur relatively fast



# Kinks in Na Diffusion Profiles Observed in Type I Silica Glass Pre-Annealed at High Temperatures I

- occurrence of kinks can be linked to an uptake of water by the silica glass (Infrasil 302) during pre-annealing
- water uptake at high temperatures can be described by a parabolic rate law
- as stated before, the location of the kink in type C profiles changes with the pre-annealing time following a parabolic rate law, see the figure at the right
- activation energies for kink displacements:
  - in wet air:  $156.9 \pm 7.0$  kJ/mol
  - in common air:  $183.4 \pm 6.3$  kJ/mol



# Kinks in Na Diffusion Profiles Observed in Type I Silica Glass Pre-Annealed at High Temperatures II

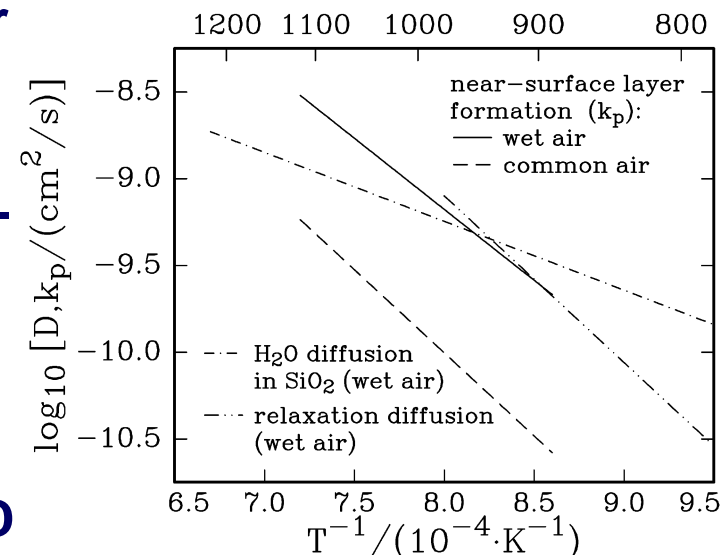
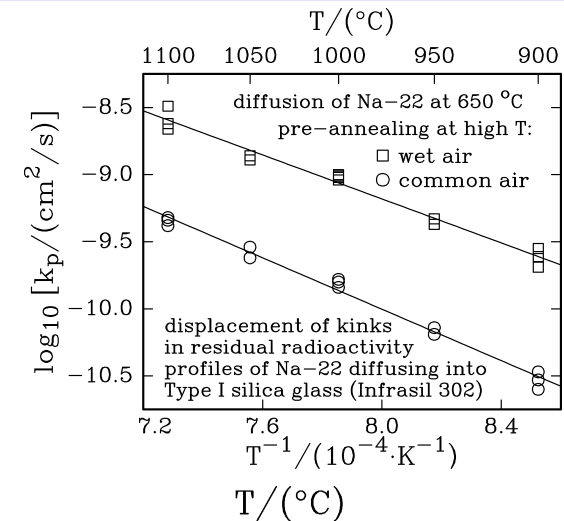
- **conclusions:**

- water is responsible for changes in sodium tracer diffusion coefficients near the surface
- following ideas by Tomozawa, a structural relaxation occurs upon the incorporation of water into silica glass, leading to changes of structure-sensitive properties, including the diffusion of Na

- **activation energy for the diffusion of water in silica 76 kJ/mol, i.e., much smaller than that observed for the kink displacement**

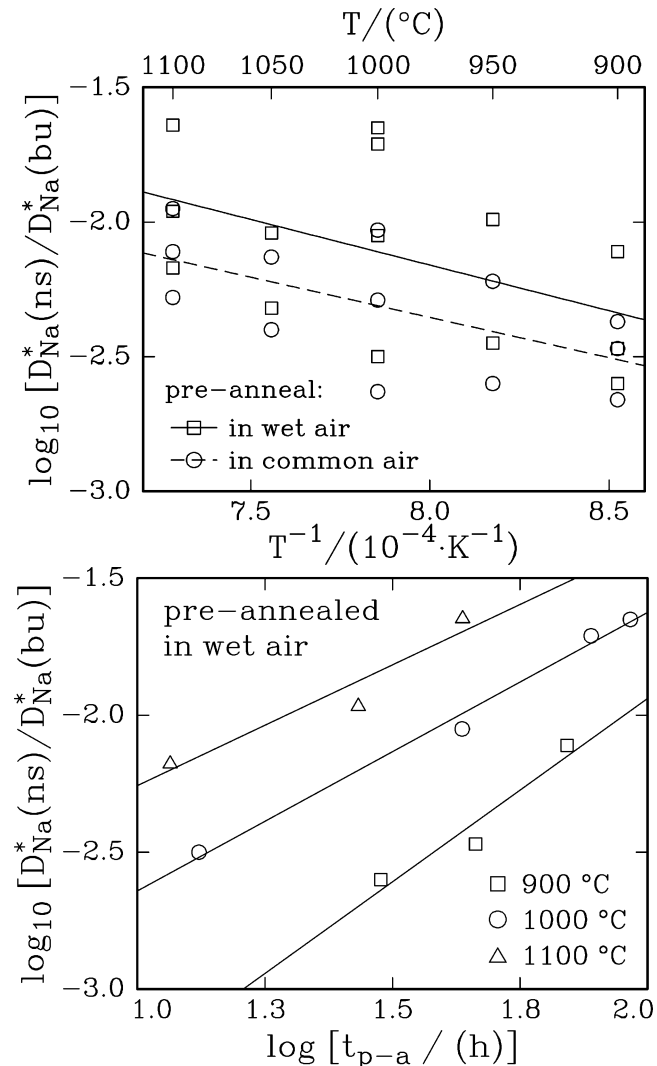
- **activation energy differences to be attributed to structural relaxation processes occurring upon the incorporation of water**

- **good agreement with data obtained by Tomozawa for structural relaxation in the form of a relaxation diffusion coefficient, D**



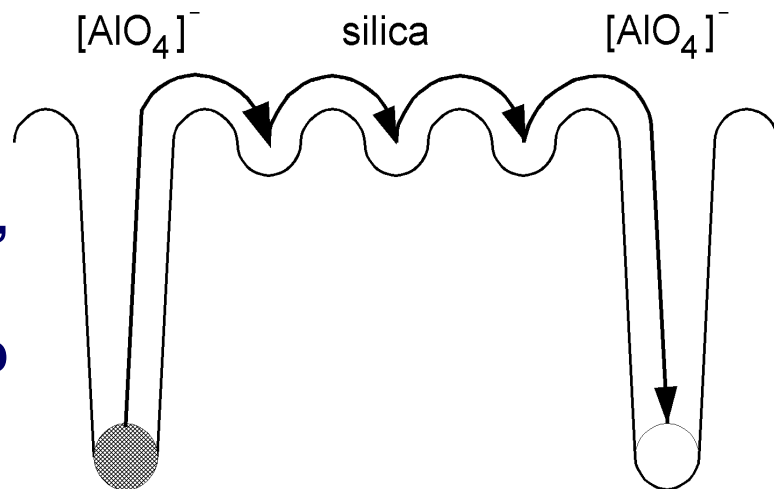
# Comparison Between the Diffusion Rate of Na in the Near-Surface Region and in the Bulk of Type I Silica Glass

- $D_{\text{Na}}(\text{ns})/D_{\text{Na}}(\text{bu})$  about 1/300 to 1/100
- values for the ratio  $D_{\text{Na}}(\text{ns})/D_{\text{Na}}(\text{bu})$  scatter very strongly
- the amount of water incorporated seems not to have any significant influence
- surprise when plotting the ratios obtained for different pre-annealing temperatures as a function of the pre-annealing time: the ratio seems to increase as a function of the annealing time
- reasons behind not yet understood; may be related to different processes involved in structural changes occurring upon the uptake of water during pre-annealing
- need additional data for shorter and longer pre-annealing times



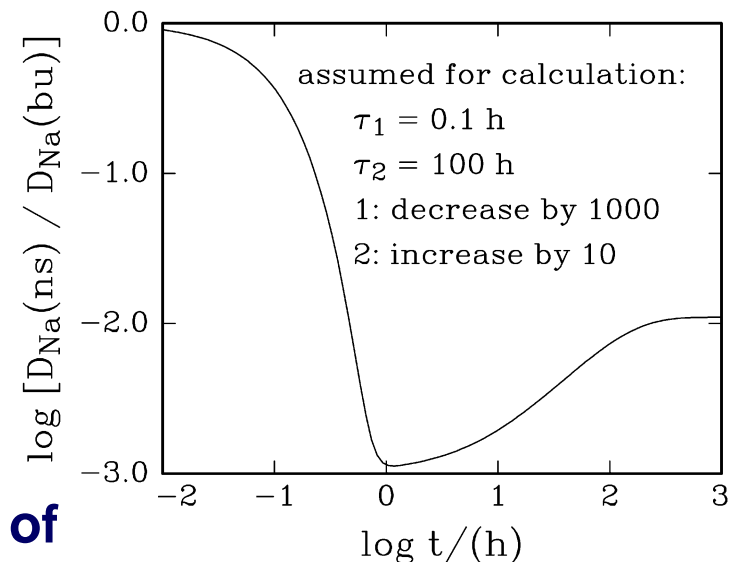
# Mechanism of the Diffusion of Na in Infrasil 302 Type I Silica Glass

- majority impurity: Al (about 30 ppma); expected to be located to a very large extent on Si sites
- Na present at a level of 1 ppma
- estimate on the spacing between Al in  $[\text{AlO}_4]^-$  groups (= “traps”) assuming a uniform distribution: 26 nm
- trapping of  $\text{Na}^+$  at  $[\text{AlO}_4]^-$  groups, which carry a negative excess charge, expected
- migration of  $\text{Na}^+$  then from trap to trap through “interstitial sites” in silica glass at a very high rate



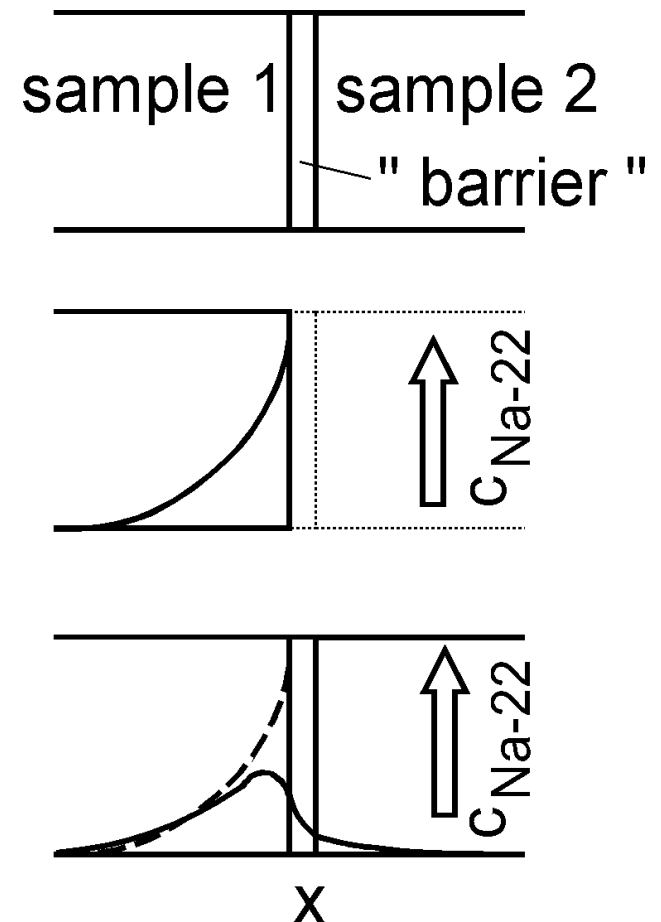
# Structural Relaxation in Type I Silica Glass

- the reduction in the sodium diffusivity in near-surface region after pre-annealing in moist atmospheres is attributed to a structural relaxation
- reaction between water incorporated into glass
$$\text{R}-\text{O}-\text{R}' + \text{H}_2\text{O} \rightleftharpoons \text{R}-\text{O}-\text{H} + \text{R}'-\text{O}-\text{H}$$
- equilibrium is dynamic and allows for a “water-assisted” relaxation processes
- to explain the observed time-dependence of  $D_{\text{Na}}(\text{ns})/D_{\text{Na}}(\text{bu})$  two relaxation processes must be present; speculation:
  - fast relaxation around  $[\text{AlO}_4]^-$  units, leading to a very significant reduction of  $D_{\text{Na}}(\text{ns})/D_{\text{Na}}(\text{bu})$
  - slow relaxation in the rest of the glass, leading to an increase of  $D_{\text{Na}}(\text{ns})/D_{\text{Na}}(\text{bu})$



# Characterization of the Effectiveness of Diffusion Barrier Layers

- sandwich of two samples with a “barrier layer” between them used
- first: generation of a tracer diffusion profile in Sample 1 by diffusion annealing at high temperature
- then generation of a “barrier layer” at the surface of Sample 2, e.g., by deposition, annealing in wet air, etc.
- then diffusion anneal of the sandwich, leading to a redistribution of the tracer
- after that, analysis of the resulting tracer distribution, e.g., by measuring a residual radioactivity profile
- diffusion mathematics needed for the data analysis worked out for different tracer distributions in Sample 1 before annealing the sandwich; the math is relatively complex



# Principles of Diffusion Mathematics

- equations governing the diffusion in Sample 1 and in Sample 2

$$\frac{\partial c_1}{\partial t} = D_1^* \cdot \frac{\partial^2 c_1}{\partial x^2} \quad x < 0 \quad \text{and} \quad \frac{\partial c_2}{\partial t} = D_2^* \cdot \frac{\partial^2 c_2}{\partial x^2} \quad x > 0$$

- regions  $x > 0$  and  $x < 0$  connected by the condition of continuity of flux at  $x = 0$ , i.e.,

$$D_1^* \cdot \frac{\partial c_1}{\partial x} \bigg|_{x=0^-} = D_2^* \cdot \frac{\partial c_2}{\partial x} \bigg|_{x=0^+} = -k_i \cdot (c_1|_{x=0^-} - c_2|_{x=0^+})$$

- $k_i$  is a rate constant for the transfer of the diffusing species across the “barrier layer”
- diffusion equations to be solved taking into account the initial tracer distribution in Sample 1,  $g(x)$ , e.g., given by the thin film solution of Fick’s second law, i.e.,

$$g(x) = c_1(x < 0, t = 0) = \frac{q}{\sqrt{\pi \cdot D_1^* \cdot t_0}} \cdot \exp\left(-\frac{x^2}{4 D_1^* \cdot t_0}\right)$$

- $t_0$  is the diffusion time of the first anneal with Sample 1 only



# Equations for Concentration Profile

- equation for the concentration in Sample 1 ( $x < 0$ ) as a function of  $x$  and  $t$ :

$$c_1(x, t) = \frac{q}{\sqrt{\pi \cdot D_1^* \cdot (t + t_0)}} \cdot \exp\left(-\frac{x^2}{4D_1^* \cdot (t + t_0)}\right) + \int_0^t \frac{\exp\left(-\frac{x^2}{4D_1^* \cdot (t - \tau)}\right)}{\sqrt{\pi \cdot D_1^* \cdot (t - \tau)}} \cdot \varphi(\tau) \cdot d\tau$$

- equation for the concentration in Sample 2 ( $x > 0$ ) as a function of  $x$  and  $t$ :

$$c_2(x, t) = -\int_0^t \frac{\exp\left(-\frac{x^2}{4D_2^* \cdot (t - \tau)}\right)}{\sqrt{\pi \cdot D_2^* \cdot (t - \tau)}} \cdot \varphi(\tau) \cdot d\tau$$

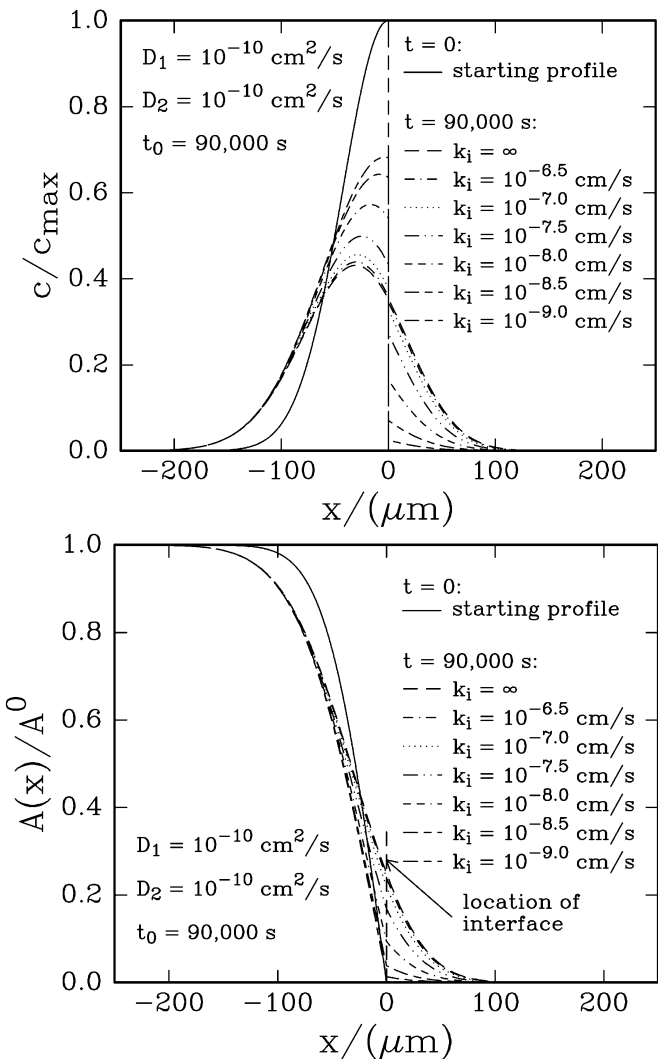
- equation for the function  $\varphi(\tau)$ :

$$\varphi(\tau) = \frac{k_i \cdot q}{\sqrt{D_1^*}} \cdot \left[ -\frac{1}{\sqrt{t + t_0}} + 2 \left( 1 + \sqrt{\frac{D_1^*}{D_2^*}} \right) \cdot \frac{k_i}{\sqrt{\pi \cdot D_1^*}} \cdot \sin^{-1} \sqrt{\frac{t}{t + t_0}} \right. \\ \left. - \left( 1 + \sqrt{\frac{D_1^*}{D_2^*}} \right)^2 \cdot \frac{k_i^2 \cdot \sqrt{t_0}}{D_1^*} \cdot \int_0^{t/t_0} \frac{1}{\sqrt{1 + T'}} \cdot \exp \left\{ \left( 1 + \sqrt{\frac{D_1^*}{D_2^*}} \right)^2 \cdot \frac{k_i^2 \cdot t_0}{D_1^*} \cdot \left( \frac{t}{t_0} - T' \right) \right\} \right. \\ \left. \cdot \operatorname{erfc} \left\{ \left( 1 + \sqrt{\frac{D_1^*}{D_2^*}} \right) \cdot k_i \cdot \sqrt{\frac{t_0}{D_1^*} \cdot \left( \frac{t}{t_0} - T' \right)} \right\} \cdot dT' \right]$$

- numerical solution of integrals of these functions used for calculating residual radioactivity profiles and also for data fitting

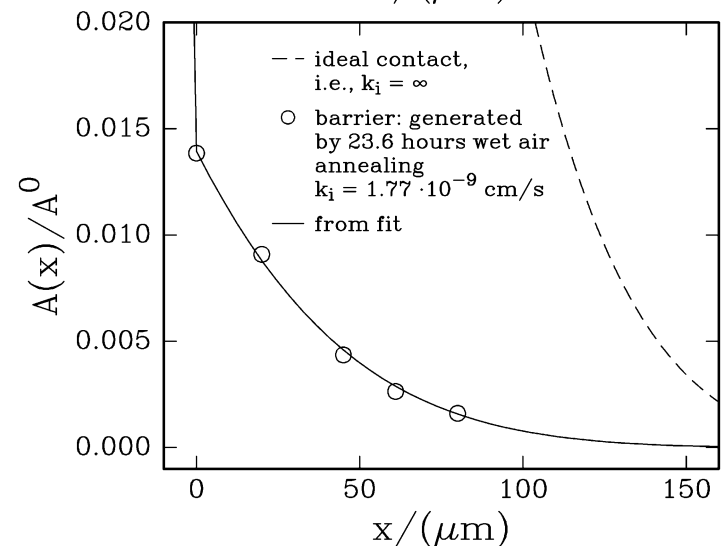
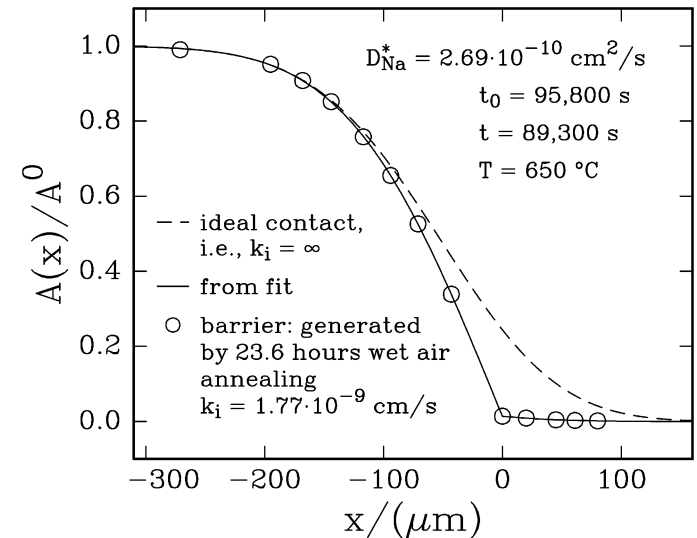
# Concentration and Residual Radioactivity Profiles

- profiles calculated for  $D_1 = D_2 = 10^{-10} \text{ cm}^2/\text{s}$  and different values of  $k_i$
- $t_0 = 90,000 \text{ s}$ ,  $t = 90,000 \text{ s}$
- top figure: initial profile after diffusion anneal of Sample 1 only and profiles after annealing sandwiches
- bottom figure: residual radioactivity profiles corresponding to the concentration profiles shown in the top figure
- experiments: measured residual radioactivities and derived data for  $k_i$  and for  $D_1 = D_2$  from fits
- values of  $k_i$  give information on the efficiency of a barrier



# Experimental Observations 23.6 h

- annealing of Sample 1 at 650 °C in common air for about 1 day for generating the initial tracer concentration profile
- annealing of Sample 2 in wet air for 23.6 hours in wet air for modification of the near-surface layer
- then diffusion anneal of sandwich for about 1 day
- top figure: overall residual radioactivity profile
- bottom figure: magnified part of the same figure in the region  $x > 0$
- solid lines: from fit of the equation discussed before to the experimental data



# Experimental Observations II

- experiments performed with four different times for the water incorporation times into Sample 2

water uptake time (h)	$\log [D_{\text{Na}}/(\text{cm}^2/\text{s})]$	$\log [k_i/(\text{cm}/\text{s})]$
11.4	$-9.527 \pm 0.004$	$-8.568 \pm 0.097$
23.6	$-9.571 \pm 0.001$	$-8.752 \pm 0.033$
50.2	$-9.564 \pm 0.001$	$-8.907 \pm 0.085$
86.3	$-9.484 \pm 0.003$	$-9.094 \pm 0.228$

- Na-diffusion coefficients very consistent
- values for  $D_{\text{Na}}$  in very good agreement with results from separate tracer diffusion experiments at 650 °C
- values for  $k_i$  decrease with increasing water uptake time, corresponding to an increasing barrier layer thickness
- also experiments with  $\text{SiO}_2$  CVD films as barrier layers and with (very ineffective) barrier layers generated by RCA-cleaning

# Analysis of the Pre-Annealing Time Dependence of $k_i$

- average sodium tracer diffusion coefficient in the barrier layer,  $D_{\text{bar}}$ :

$$D_{\text{bar}} = k_i \cdot d_{\text{bar}}$$

$d_{\text{bar}}$  = barrier thickness,  $k_i$  = rate constant for transfer of Na across the barrier

- flux of Na across barrier layer:

$$j_{\text{Na}} = k_i \cdot \Delta c_{\text{Na}} = D_{\text{bar}} \cdot \frac{\Delta c_{\text{Na}}}{d_{\text{bar}}}$$

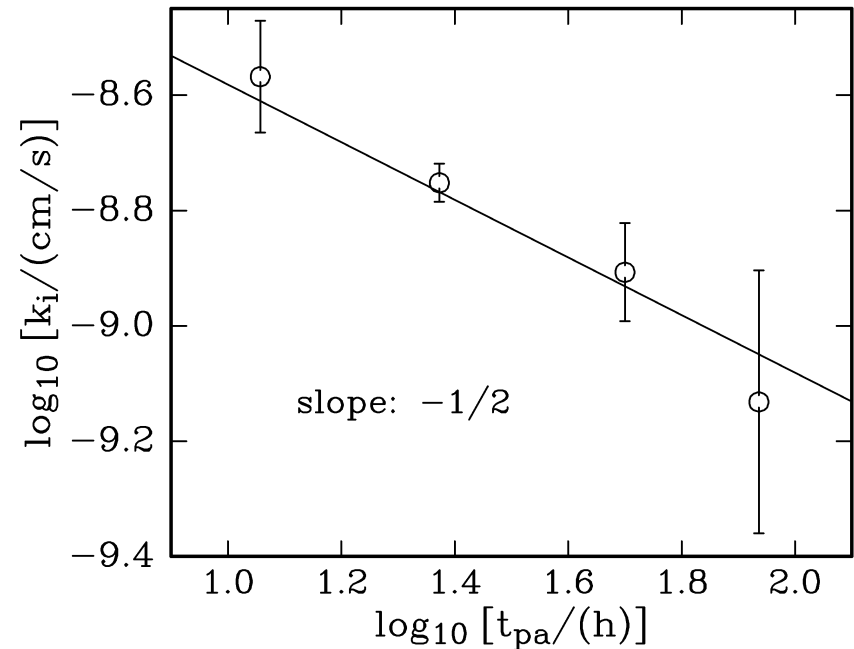
- thickness of barrier layer:

$$d_{\text{bar}} = \sqrt{k_p \cdot t_{\text{pa}}}$$

$k_p$  = parabolic rate constant for the near-surface layer generation

- relation between  $k_i$  and the pre-annealing time,  $t_{\text{pa}}$ :

$$k_i = \frac{D_{\text{bar}}}{\sqrt{k_p}} \cdot t_{\text{pa}}^{-1/2}$$



values determined experimentally for  $k_i$  are by a factor of about 2 larger than values predicted for  $k_i$  by using values for  $k_p$  and for  $D_{\text{Na}}$  from separate experiments - it is unknown why this is so

# CONCLUSIONS

- **silicate glasses (e.g., Infrasil 302 and Corning Code 1737 glass) may take up water from the environment during high temperature annealing in air containing some water, i.e., they are “thirsty”**
- **the water uptake follows a parabolic rate law, i.e., it is to a large extent diffusion controlled**
- **water-assisted structural changes are believed to occur as a result of the water uptake**
  - **leads to a modification of glass properties near the surface**
  - **causes a decrease in the mobility of sodium ions in the near-surface region**
- **opens the possibility to make “functionally graded” glass**
- **example: generation of a sodium diffusion barrier layer on Corning Code 1737 glass**

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